Synthesis and photoelectrochemical properties of a self-assembled monolayer of a ferrocene–porphyrin–fullerene triad on a gold electrode

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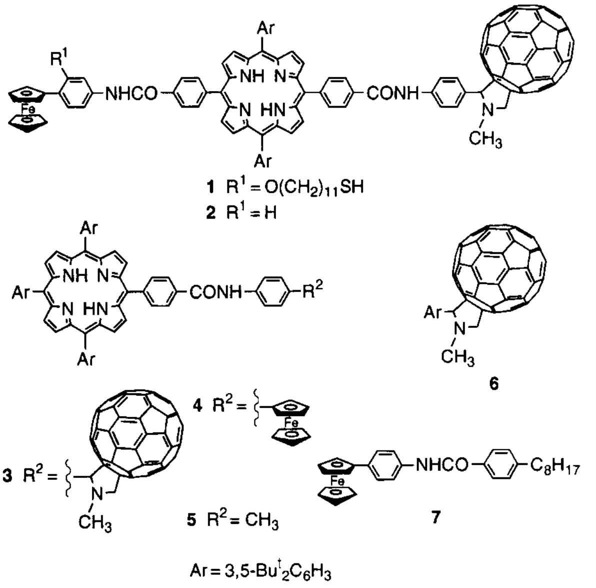
A self-assembled monolayer of a ferrocene–porphyrin–C_{60} triad has been prepared to mimic efficient vectorial electron transport across a photosynthetic membrane.

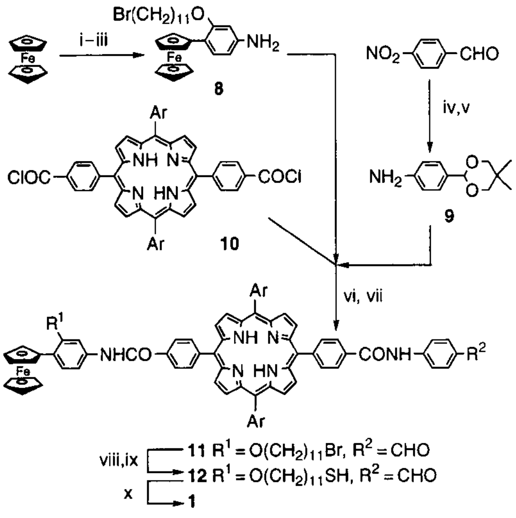
In photosynthesis a key process for the conversion of light to chemical energy is initial electron transfer (ET) events in the reaction center complex. The ultrafast and unidirectional multistep ET takes place along well-arranged pigments embedded in the transmembrane proteins, leading to a generation of a charge-separated state across the membrane with a quantum efficiency (Φ) of nearly 100%. There have been numerous synthetic attempts to mimic this highly efficient process. Some of them, such as triads, tetrads, and pentads, produce a long-lived, charge-separated state with a high quantum yield.[1] However, efficient conversion (overall Φ = 1–10%) of light to photocurrents or chemical products *via* the charge-separated state has been hampered, because of the difficulty of assembling the donor–acceptor linked molecules unidirectionally in artificial membranes such as lipid bilayer and Langmuir–Blodgett membranes.[2–4] Self-assembled monolayers (SAMs)[5] are an alternative and promising approach to organize the donor–acceptor molecules on electrodes owing to their uniform and well-ordered structures.[6,7] Here we report the first preparation and photoelectrochemical properties of a SAM of a ferrocene (Fc)–porphyrin (P)–C_{60} triad **1** on a gold electrode.



The synthetic route to **1** is shown in Scheme 1. Aminophenylferrocene **8** was prepared in three steps from ferrocene. Formyl-protected aniline **9** was synthesized in two steps from 4-nitrobenzaldehyde. Cross-condensation of porphyrin bis(acid chloride) **10** with **8** and **9** in benzene in the presence of pyridine, followed by acidic hydrolysis, afforded ferrocene–prophyrin **11** in 23% yield.[8] Bromide **11** was converted to thiol **12** *via* thioesterification with potassium thioacetate and subsequent base deprotection. The triad **1** was obtained by 1,3-dipolar cycloaddition using **12**, *N*-methylglycine, and C_{60} in toluene in 54% yield.[9] The reference compounds **2**–**7** were also prepared. Their structures were verified by spectroscopic analyses including ^{1}H NMR and MALDI-TOF mass spectra.†

The absorption spectrum of **2** in THF is essentially a linear combination of those of **5**, **6** and **7**, indicating no evidence for strong interaction among these chromophores. Absorption due to the porphyrin is much stronger relative to the C_{60} and the ferrocene, showing that the porphyrin is a major absorber of photons. Fluorescence spectra of **2** and **3** in THF are quenched strongly as compared with that of **5** when excited at the Soret band under the same concentration (relative intensities: 0.14 for **2**, 0.19 for **3**). In contrast, the relative fluorescence intensity of **4** *vs.* **5** (0.60) is much larger, suggesting that quenching of the excited singlet porphyrin (^{1}P*) by the attached C_{60} is a dominant deactivation pathway in **1**.

A cyclic voltammetric experiment using **1** on Au in CH_2Cl_2 containing 0.1 M $Bu^n{}_4NPF_6$ electrolyte with a sweep rate of 100 mV s^{-1} was performed to estimate the surface coverage. The adsorbed amount of **1** on Au was calculated from the charge of the anodic peak of the ferrocene to be 1.9×10^{-10} mol cm^{-2} (86 Å^2 molecule^{-1}), which is comparable to the porphyrin–polyalkanethiols ($0.8\text{–}2.0 \times 10^{-10}$ mol cm^{-2})[7,10] and C_{60}–polyalkanethiols ($1.3\text{–}2.0 \times 10^{-10}$ mol cm^{-2})[11,12] on gold electrodes. Assuming that the triad is packed perpendicularly to the gold surface, then the occupied area of one molecule is calculated to be *ca.* 87 Å^2 for hexagonal packing of the C_{60} moieties, which is consistent with the experimental value. Therefore, we can conclude that the triad molecules are well-packed with almost perpendicular orientation on the gold surface.



Scheme 1 *Reagents and conditions*: i, H_2SO_4, 2-amino-5-nitrophenol, 13%; ii, 1,11-dibromoundecane, K_2CO_3, 88%; iii, H_2, Pd/C, 84%; iv, neopentyl glycol, TsOH, 95%; v, H_2, Pd/C, 69%; vi, pyridine; vii, TFA, H_2SO_4, 23% (2 steps); viii, potassium thioacetate, 81%; ix, KOH, 50%; x, *N*-methylglycine, C_{60}, 54%.

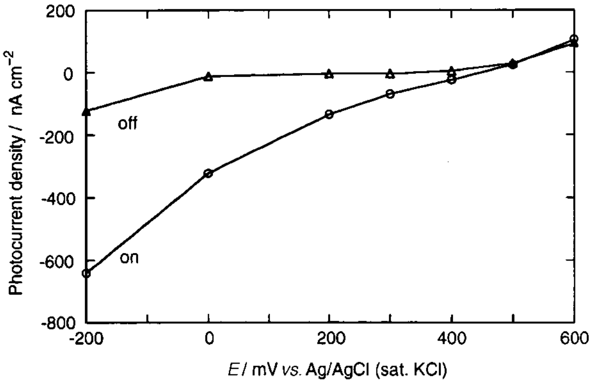


Fig. 1 Photocurrent *vs.* applied potential curves for the triad cell when the light is on (○) and off (△): λ = 438.5 nm (60 μW cm^{-2}), O_2-saturated 0.1 M Na_2SO_4 solution.

Photoelectrochemical measurements using **1** on Au in a three electrode system were carried out in an oxygen-saturated 0.1 M Na_2SO_4 solution. Fig. 1 shows current–potential curves under an illumination of 438.5 (±4.9) nm light (60 μW cm^{-2}). The SAM showed a photoelectrochemical response when the light was switched on and off. The photocurrent was reduced by argon bubbling of the solution and recovered to the initial state by successive oxygen bubbling. The results indicate that $C_{60}^{\cdot-}$ gives an electron to O_2 to produce $O_2^{\cdot-}$.[6] The intensity of the photocurrent in the present system is larger by two orders of magnitude than that of the porphyrin–polyalkanethiol systems,[10] implying that the C_{60} and ferrocene moieties are responsible for the higher efficiency. An increase in the cathodic photocurrent with an increase of the negative bias to the gold electrode demonstrates that the photocurrent flows from the gold electrode to the counter electrode through the electrolyte. The cathodic photocurrent dramatically increased as the potential applied dropped below +500 mV, which is in good agreement with the redox potential of ferrocene [+0.51 V ($Fc/Fc^{\cdot+}$)] (Fig. 1). This indicates that the photocurrent generation is controlled by the ET rate between the gold electrode and the ferrocene, similar to the porphyrin–ferrocene SAM system.[7] When methyl viologen (MV^{2+}) was employed as an electron carrier, the time profile of the photocurrent was dependent on the concentration of MV^{2+}. The initial and stable photocurrents increased with an increase of the MV^{2+} concentration under the argon- or oxygen-saturated conditions, implying that MV^{2+} also accepts an electron from $C_{60}^{\cdot-}$ to generate $MV^{\cdot+}$.

In the absorption spectra the Soret band of **1** on Au in air using the transmission mode is broad and red-shifted by 11 nm, compared with that of **2** in THF. This behavior is similar to that of the polymethylenethiol-linked porphyrin systems on gold electrodes.[7,10] This suggests increased π–π interaction among the porphyrin moieties within the SAM, which is quite consistent with the results obtained using cyclic voltammetry. The action spectrum of the cell roughly agrees with the absorption spectrum of **1** on Au, indicating that the porphyrin is the major photoactive species for photocurrent generation.

Quantum efficiency based on the number of photons absorbed by **1** on Au was calculated using the input power (60 μW cm^{-2} at 438.5 nm), the photocurrent density, and the estimated absorbance on Au (0.059). Under the optimal conditions using the oxygen-saturated solution with 30 mM MV^{2+}, we obtained a net photocurrent density of 660 nA cm^{-2} at −200 mV from the triad cell. Thus, the quantum yield is found to be 25%, which is more than two times larger than the highest value (11%) among the previous reports of photosynthetic multistep ET across artificial membranes and at monolayer-modified metal electrodes.[2–4,6,7,10,12]

The photocurrent generation may be explained as follows. On the basis of the fluorescence quenching experiments together with previously reported results,[6,13,14] photoinduced ET or charge-transfer occurs from $^1P^*$ [−0.82 V ($^1P^*/P^{\cdot+}$)] to C_{60} [−0.64 V($C_{60}/C_{60}^{\cdot-}$)] rather than from Fc to $^1P^*$. The resulting $C_{60}^{\cdot-}$ transfers an electron to diffusing electron carriers such as oxygen [−0.48 V ($O_2/O_2^{\cdot-}$)] and/or MV^{+2} [−0.62 V $MV^{+2}/MV^{\cdot+}$)], which eventually give an electron to the counter electrode. On the other hand, successive charge shift (CSH) occurs from Fc to $P^{\cdot+}$ [+1.08 V ($P/P^{\cdot+}$)], then from the gold electrode to $Fc^{\cdot+}$, resulting in the recovery of the initial state and a net vectorial electron flow from the gold electrode to the counter electrode through the monolayer and the electrolyte. There is a plausible explanation for the remarkable high efficiency in the system. We have shown that $^1P^*$ within the SAM on gold electrodes is strongly quenched by the gold electrodes.[10] This means that (i) initial photoinduced ET from $^1P^*$ to the first acceptor must compete with deactivation due to the gold electrode and (ii) the CSH to the second acceptor is much faster than charge recombination to the ground state. Utilization of C_{60} with its small reorganization energy may fully satisfy these requirements and improve the quantum yield greatly.[6,12,13,15]

In conclusion, a SAM of a ferrocene–porphyrin–C_{60} has been prepared for the first time. The high quantum yield implies that a combination of fullerenes and SAMs is promising for applications in materials science. Although our interpretation of the photocurrent generation mechanism is consistent with the results obtained by the electrochemical and photoelectrochemical measurements, further details must await photodynamical experiments in solutions and on a gold surface as well as structural studies on the monolayer.

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Notes and references

† *Selected data* for **1**: δ_H(270 Mz; $CDCl_3$) 8.89 (d, *J* 5, 2H), 8.88 (d, *J* 5, 2H), 8.80 (d, *J* 5, 2H), 8.76 (d, *J* 5, 2H), 8.71 (br s, 1H), 8.36 (d, *J* 8, 2H), 8.29 (d, *J* 8, 4H), 8.20 (d, *J* 8, 2H), 8.19 (br s, 1H), 8.05 (s, 4H), 7.97 (d, *J* 8, 2H), 7.81 (s, 2H), 7.74 (s, 1H), 7.67 (br s, 2H), 7.58 (d, *J* 8, 1H), 7.10 (d, *J* 8, 1H), 4.85 (s, 2H), 4.63 (d, *J* 10, 1H), 4.43 (s, 1H), 4.30 (s, 2H), 4.18 (t, *J* 7, 2H), 4.09 (s, 5H), 3.82 (d, *J* 10, 1H), 2.69 (s, 3H), 2.53 (q, *J* 7, 2H, CH_2SH), 1.99 (quintet, *J*, 2H), 1.7–1.2 (m, 53H), −2.80 (br s, 2H).

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